

# PATENT SPECIFICATION

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## (54) SURFACE-PATTERNED, SURFACE-ACTIVATED POLYMER FILM

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymer film and more particularly to surface-patterned and surface-activated polymer film.

The treatment of perfluorocarbon polymer film with electrostatic discharge to render its surface adherent is disclosed in U.S. Patent Specification No. 3,296,011. The embossing of polycarbonate tape to reduce its coefficient of friction and permit penetration of oil is disclosed in U.S. Patent Specification No. 3,105,872.

The present invention involves the discovery that by combining treatments of this sort, a polymer film is obtained which is especially suited for use in polymer tape/oil insulation systems. Accordingly the present invention provides a polymer film, at least one surface of which has been surface activated by chemical etching or electrostatic discharge treatment and at least one surface of which has a surface pattern thereon which is in the form of (a) a multiplicity of grooves each of which extends from at least one edge of the film or (b) a multiplicity of ribs each of which extends from at least one edge of the film, the said grooves or ribs extending in a generally transverse direction across the film.

The surface pattern acts to permit the penetration of oil in between layers of tape formed from the film to displace all air bubbles, for the purpose of forming such electrical insulation. The surface activation of the polymer film increases the affinity of the oil and polymer film for one another to give improved electrical performance for the insulation.

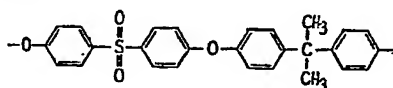
The polymer from which the film is made

can be any polymer which has the electrical, chemical and physical properties desired for a particular application. Thus, for example the polymer should have sufficient mechanical strength to withstand fabrication into an insulation system and its use. The polymer should also have sufficient thermal stability and high melting point to withstand the temperature of the fabrication and use. For electrical uses, the polymer should be a dielectric with a degree of electrical non-conductivity suitable for the voltage stress to be withstood. Examples of polymer from which the film of the invention can be made include the fluorocarbon polymers wherein the polymer chain consists essentially of carbon atoms or carbon atoms and ether groups and the ratio of fluorine atoms on the chain to carbon atoms in the chain is an average of at least 1:1, usually an average of at least 1.5:1. Examples of fluorocarbon polymers include the polymers of chlorotrifluoroethylene and tetrafluoroethylene, for example polychlorotrifluoroethylene itself, polytetrafluoroethylene itself and copolymers of tetrafluoroethylene with less than 35 percent by weight based on total polymer weight of one or more copolymerizable monomers such as ethylene, ethylene and hexafluoroacetone as disclosed in U.S. Patent Specification No. 3,342,777, ethylene and other vinyl monomers as disclosed in German Patent Publication No. 1,957,963, hexafluoropropylene as disclosed in U.S. Patent Specifications Nos. 3,085,083 and 2,946,763, higher perfluoroalkanes such as those containing from 4 to 10 carbon atoms, perfluoro(alkyl vinyl ethers) such as perfluoro - (ethyl- or propyl vinyl ether) disclosed in U.S. Patent Specification No. 3,123,123, perfluoro - (2 - methylene - 4 - methyl - 1,3 - dioxolane) as disclosed in U.S. Patent Specification No. 3,308,107, and the highly fluorinated monomers in which a single hydrogen is present and does not change the fluorocarbon character of the copolymer, such monomers being for example the 2-hydroperfluoroalkenes containing 2 or 3 car-

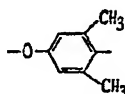
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bon atoms such as 2-hydropentafluoropropene, the omega-hydropentafluoroalkenes containing from 3 to 10 carbon atoms, and the omega-hydropentafluoro(alkyl vinyl ethers) in which the alkyl group contains from 1 to 5 carbon atoms.

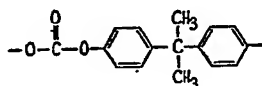
- 5 Additional examples of polymers from which tape can be made include polyolefins such as polyethylene, polypropylene, and poly - 4 - methylpentene; polysulfones such as those consisting essentially of the recurring unit



- 15 polyphenylene oxides, such as those consisting essentially of the recurring unit



and polycarbonates such as those consisting essentially of the recurring unit



- 20 and polyethylene terephthalate.

- When the film is to be used as tape wrapping to form the primary electrical insulation in an electrical cable, the polymer from which the tape is made preferably has a dielectric constant which is no greater than 4.0 and a dissipation factor of no greater than 0.002. The dielectric constant values used herein are measured at 20°C. unless otherwise specified, and the dissipation factor values used herein are measured at 100°C. and a voltage stress of 100 volts/mil unless otherwise specified. The more preferred dielectric constant and dissipation factor for the polymer are no greater than 3.0 and 0.001, respectively. For other electrical applications, such as in capacitors, the polymer can have higher dielectric constant values to promote electrical storage capacity. Film can be formed from these polymers and can be oriented if desired by conventional procedures. Typically, the film will be from 1 to 15 mils thick.

- The film is then subjected to a suitable surface patterning operation and a suitable surface-activating operation. Alternatively, the film may be formed with a pattern on one or both of its surfaces by a casting process or by the moulding process disclosed in U.S. Patent Specification No. 3,515,778 (Fields *et al*) and then the surface-activating operation may be effected. The film may be severed into various shapes (the most useful being strips which can be used as the tape in tape/oil insulation)

before or after being subjected to the patterning or activating operation(s).

With respect to the tape form of the film, the surface pattern can be any suitable visually observable pattern formed on one or both surfaces of the tape. Preferably, the pattern comprises a multiplicity of grooves extending from at least one edge of the tape across at least one surface thereof. This facilitates penetration of oil inwardly from the edge of the tape when the tape is used to form a tape/oil insulation. One example of such a pattern is depicted in Fig. 2 of U.S. Patent Specification No. 3,077,510 (Olds) in which the pattern consists of a multiplicity of parallel grooves on one surface of the tape extending at an angle to both axes of the tape. Another example of a suitable pattern is depicted in Fig. 3 of U.S. Patent Specification No. 3,263,020 (Thevenon) in which the pattern consists of transverse notches on one surface of the tape. Still another example of a suitable pattern is depicted in Figs. 2 and 3 of U.S. Patent Specification No. 3,105,872 (Thompson *et al*) wherein the pattern consists of a random disposition of hills and valleys complementarily formed on both surfaces of the tape, with the valleys forming random channels across the width of the tape. Still another useful pattern is depicted in Figs. 3 and 4 of U.S. Patent Specification No. 3,430,116 (Johnstone), wherein the pattern consists of intersecting grooves on one surface of the tape and complementarily intersecting ridges on the opposite surface of the tape. The aforementioned Figs. are incorporated by reference herein to illustrate some of the various patterns which can be used in the present invention. The Patent Specifications containing these Figs. can also be referred to for methods of making the patterned tapes. The same methods are applicable to forming the pattern in a film which is subsequently severed into tape.

Another pattern which can be used is wherein the tape possesses transverse ribs extending from one surface of the tape, with the ribs being 10 mils wide and 2 mils high and being on 100 mil centers. Tape (or film) with this pattern can be made by the aforementioned Fields *et al*. process.

Any chemical etch or electrostatic discharge method for surface-activating the polymer tape can be used.

One chemical etch method for surface activating the polymer tape is to etch the surface (usually both surfaces) of the tape, for example, according to the procedure disclosed in U.S. Patent Specifications Nos. 2,789,063 (Purvis and Beck) and 2,809,130 (Rappaport), the sodium etch being the preferred chemical etch. The chemical etch, briefly, is conducted by contacting the surface of the tape with a solution of an alkali metal in liquid ammonia or with an alkali metal polyaryl hydrocarbon-

solvent solution such as sodium naphthalene in dimethyl glycol ether at a temperature at which reaction between the alkali metal and tape composition occurs and for a time which substantially confines the etch to the surface of the tape only. Generally, the tape surface is sufficiently etched after only a few seconds of contact with the etching solution and the surface pattern in the tape prior to etching is still recognizable.

Another method for surface activating the polymer tape is to subject its surface to electrostatic discharge which can be carried out according to the procedure described in U.S. Patent Specification No. 3,296,011 (McBride and Wolinski) under conditions at which corona occurs during the discharge and the tape surfaces are exposed to this corona. The procedure can be briefly described as passing the tape between electrodes of opposite polarity spaced 0.015 to 0.25 inches apart, applying an alternating current at a voltage of 10,000 to 30,000 volts to the high voltage electrode at a frequency of 300,000 to 500,000 cycles/sec in the presence of air of an inert atmosphere or a mixture of an inert gas and a volatile organic compound such as glycidyl methacrylate. The time of exposure of the tape to the electrostatic discharge will depend on the conditions used and polymer from which the tape is made. Typically, exposure times of 1 to 120 seconds will suffice.

These surface-activating treatments can be applied to only one surface of the tape but more often will be applied to both surfaces. These treatments can also be applied to film which is then severed into the tape form.

The resultant surface-patterned surface-activated tape can be used to form polymer tape/oil insulation systems according to conventional procedures. For example, in the case of an electrical cable, the insulation is usually formed by helically wrapping the tape about the inner conductor of the cable to form a multiplicity of layers, e.g. 100 layers, of the polymer tape, followed by forming the outer conductor around the outermost layer of the insulation. The resultant cable is then usually subjected to vacuum to remove all air from the insulation system followed by addition of a dielectric oil, such as silicone oil, polybutene oil, or mineral oil, to displace any remaining air bubbles from the system. The pattern on the surface(s) of the tape facilitates complete penetration of the oil into and between the layers of tape wrapping. In subsequent use of the cable, the surface activation of the tape leads to improved electrical performance of the cable manifested by the dissipation factor of the insulation system being lower during long term use than if the surface activation were omitted. This improvement comes from the improved affinity of the oil for the polymer tape by virtue of the surface activation of the latter.

To reduce the tendency of the tape to wrinkle in forming the tape/oil insulation system, the tape can be pre-coated with dielectric oil and the pre-coated tape used in the wrapping operation.

By way of example, the ribbed tape hereinbefore described having a total thickness of 5 mils can be surface activated by the following procedures:

The tape made of tetrafluoroethylene-hexafluoropropylene copolymer (about 16% by weight hexafluoropropylene) is subjected (both surfaces) to electrostatic discharge essentially according to the procedure of Example 1 of the aforesaid U.S. Patent Specification No. 3,296,011. The surface activation obtained is indicated by the spreading coefficient of the tape in combination with polybutene oil increasing from  $-14.2$  ergs/cm.<sup>2</sup> for the untreated tape to  $-1.2$  ergs/cm.<sup>2</sup> for the surface-activated tape.

Tapes of polyethylene, polycarbonate, and polyethylene terephthalate may be exposed to electrostatic discharge using the following apparatus and procedure.

The apparatus consists of a base electrode in the form of a horizontal stainless steel drum  $4 \frac{3}{8}$  inches in diameter and 10 inches long, rotatable on its axis. Covering the base electrode in close contact is a dielectric layer of FEP (fluorinated ethylene propylene copolymer) of 20 mils thickness. A high voltage electrode 6 inches long is horizontally disposed parallel to the axis of the base electrode so that it presents a  $\frac{1}{4}$  inch wide flat face toward the base electrode. The face of the high voltage electrode is separated from the dielectric covering layer by a gap of 40 mils. A polymer film (short length of tape) to be treated is stretched tightly over the dielectric covering layer, and the drum is rotated to move the film past the high voltage electrode at a speed of 11 feet/minute. An A-C power supply providing 6500 volts at a frequency of 10,000 Hertz is applied between the above mentioned electrodes creating a corona between the high voltage electrode and the film. The film is subjected to 3 passes on each side in an air atmosphere. Surface activation of the polyethylene is indicated by its spreading coefficient increasing from  $-0.8$  ergs/cm.<sup>2</sup> to spontaneous spreading of the polybutene oil over the polymer surface. For the polycarbonate and polybutene oil, the spreading coefficient increases from  $-0.6$  ergs/cm.<sup>2</sup> to  $-0.3$  ergs/cm.<sup>2</sup>. For the polyethylene terephthalate and polybutene oil, the spreading coefficient increases from  $-1.1$  ergs/cm.<sup>2</sup> to spontaneous spreading.

Description of the spreading coefficient as increasing means that its numerical value is moving to smaller negative numbers (and correspondingly higher affinity); zero and

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positive values for spreading coefficient are referred to as spontaneous spreading.

- 5 A ribbed tape of polytetrafluoroethylene may be subjected to chemical etching by dipping the tape into a 2% solution of sodium 1-methylnaphthalene in tetrahydrofuran at room temperature for about five seconds. Surface activation of the tape is indicated by its spreading coefficient increasing from  $-10.1 \text{ ergs/cm}^2$  for the untreated
- 10 tape to  $-1.0 \text{ ergs/cm}^2$  for the etched tape.

- The procedure of the preceding paragraph may be repeated on ribbed tape of tetrafluoroethylene-hexafluoropropylene copolymer except that the etching time is about 60 seconds, and the spreading coefficient increases from  $-14.2 \text{ ergs/cm}^2$  for the untreated tape to  $-0.3 \text{ ergs/cm}^2$  for the etched tape.

- 20 Similar results are obtained when tapes or films of other polymers and other surface patterns are surface activated according to these procedures.

- 25 Preferably, the surface activation of the polymer is such that its affinity for oil is increased by at least 20% over the natural affinity (untreated polymer) of the polymer for the oil as calculated from the expression

$$\frac{S(\text{initial}) - S(\text{after surface activation})}{S(\text{initial})} \times 100$$

- 30 wherein S is the spreading coefficient in  $\text{ergs/cm}^2$ . The value of S can be calculated from the expression  $S = \gamma_r (\cos \theta - 1)$  wherein  $\gamma_r$  is the surface tension of the oil in  $\text{ergs/cm}^2$  and  $\cos \theta$  is the contact angle that a drop of the oil forms on the polymer surface.
- 35

#### WHAT WE CLAIM IS:—

1. A polymer film, at least one surface of

which has been surface-activated by chemical etching or electrostatic discharge treatment and at least one surface of which has a surface pattern thereon which is in the form of (a) a multiplicity of grooves each of which extends from at least one edge of the film or (b) a multiplicity of ribs, each of which extends from at least one edge of the film, the said grooves or ribs extending in a generally transverse direction across the film.

2. A film according to claim 1 in the form of tape.

3. A film according to claim 1 or 2 made of a fluorocarbon polymer, wherein the polymer chain consists essentially of carbon atoms or carbon atoms and ether groups and the ratio of fluorine atoms on the chain to carbon atoms in the chain is an average of at least 1:1.

4. A film according to claim 3 made of polytetrafluoroethylene.

5. A film according to claim 3 made of a tetrafluoroethylene copolymer.

6. A film according to claim 5 made of tetrafluoroethylene/hexafluoropropylene copolymer.

7. A film according to claim 1 or 2 made of polyolefin.

8. A film according to claim 1 or 2 made of polycarbonate.

9. A film according to any one of the preceding claims, both surfaces of which have been activated.

10. A film according to claim 1 or 2 substantially as described herein.

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